Electric and Dielectric Properties of Ni Substituted Mg-Zn-Cu Ferrites

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Abstract

The electrical properties of the spinel ferrite having general chemical formula $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ (where x= 0.1, 0.2, 0.3, 0.4 & 0.5) have been studied. The samples in the series were prepared by standard double sintering ceramic method. DC resistivity (ρ) measurements were carried out as a function of temperature using simple two-probe method and activation energy (ΔE) was determined. It is found that conduction is due to formation of small polarons. The Curie temperature for the samples was determined from resistivity versus temperature curve. The dielectric parameters such as dielectric constant, loss tangent were determined as a function of frequency in the range 100Hz-1MHz at room temperature. The compositions exhibit normal dielectric behaviour, which is attributed to Maxwell-Wagner type interfacial polarization. AC conductivity calculated as a function of frequency at room temperature was found to be increase with a rise in frequency exhibiting normal ferrimagnetic behaviour.

Keywords

Magnetic Materials; Ceramic Method; Dielectric Properties; Electrical Properties

Introduction

Ferrites emerge as one of the commercially important magnetic materials because of their high electrical resistivity, low eddy current losses and appropriate dielectric loss contributive to immense technological applications over wide range of frequencies [Laishram et al 1999, Naeem et al 2009]. High electrical resistivity, manufacture without much difficulty, low cost make the polycrystalline ferrite widely suitable for intermediate and high frequency electromagnetic devices.

Among various ferrites, spinel ferrite is of exceptionally significant interest due to their attractive scientific and technological features in diverse fields such as magnetic recording and separation, catalyst, photocatalyst, drug delivery, pigments, magnetic resonance imaging (MRI) etc. Regardless of these applications, spinel ferrites can also be used in many electronic devices due to their high permeability at high frequencies, high mechanical and chemical stability and reasonably low cost. The spinel ferrites are highly suitable for computer memory and logical devices, transformer cores, recording heads etc. [Bardhan et al 2010]

Microminiaturization of electronic circuits predominant in the fields of mobile communication and information technology demands electronic components with very small size [Qi et al 2002]. Recently, the passive surface mounting devices (SMD) such as microinductors and multilayer chip inductors (MLCIs) have been rapidly developed for electronic applications. Ni-Cu-Zn ferrites and Mg-Cu-Zn ferrites are appropriate for micro inductor applications that found applications in the latest electronic products such as mobile phones, video cameras, laptop, etc., and required miniaturization. Modern technological developments concerning electrical devices require higher performance of the inductor, to satisfy which, Ni-Cu-Zn [Nakamura et al 1998, Murthy et al 2002] and Mg-Cu-Zn [Haque et al 2008] ferrites are the dominant materials for these applications as Surface Mounting Device (SMDs). Furthermore, Mg-Cu-Zn ferrites are also a pertinent magnetic material for wide applications due to its high resistivity, high Curie temperature, and environmental stability as well as low cost [Roy et al 2011].

The initial permeability of a ferrite is very sensitive property for the ferrite materials [Varalaxmi et al 2011]. It is believed that increase of initial permeability can be obtained by decreasing magnetostriction constant. As the magnetostriction constant of Mg-Cu-Zn ferrite is lower than that of Ni-Cu-Zn ferrite, it was expected that higher magnetic properties would be obtained from MLCI using Mg-Cu-Zn ferrite [Bachhav et al 2011] to realize the further miniaturization than that using Ni-Cu-Zn ferrite. The Mg-Zn-Cu ferrites have advantage over Ni-Cu-Zn ferrites that they are

economical [Smith et al 1959] and easy to synthesize. Therefore, Mg-Zn-Cu ferrites with low sintering temperature have been developed as the materials for MLCIs with high-performance and low cost.

The aim of the present work is to study electrical and dielectric behaviour of Ni-Mg-Cu-Zn ferrites with Ni substitution for Mg. In this study, the measurement of DC resistivity, dielectric constant, dielectric loss tangent and AC conductivity are made on the ferrite samples having general formula $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ (where x = 0.1, 0.2, 0.3, 0.4 & 0.5), which makes better understanding on the conduction mechanism and dielectric polarization.

Experimental

In the present investigation, the ferrite samples having general formula $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ (where x= 0.1, 0.2, 0.3, 0.4 and 0.5) have been prepared by standard double sintering ceramic method [Bachhav et al 2011]. The metal oxides (Mg, Ni, Cu, Zn etc) used as the staring materials were thoroughly mixed in an agate mortar with acetone for 4h to homogenize the mixture prior to the solid state formation; and then heat-treated and compacted in the form of pellets and toroids at 8 tons per square inch using hydraulic press. During this preparation, pre-sintering at 700°C for 12h and powdering of the formed products was followed by final sintering at 1050°C for 24h in a programmable furnace and slow cooling to room temperature to yield the final product.

The DC electrical resistivity measurement of the samples was carried out using two probe methods on pellets of dimension 1.5 cm diameter and 0.3 cm thickness at temperature ranging from 300 K-873 K. Silver foils were placed on either side of the pellets for well ohmic contacts. The assembly was kept inside a furnace and the temperature was varied. The relation between resistivity and temperature [smith et al 1959] may be expressed as

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (1)$$

Where ΔE is the activation energy in (eV) for conduction, k_B is the Boltzmann constant and T is the temperature in Kelvin (K).

The dielectric parameters such as dielectric constants, loss tangent and AC conductivity were determined using LCR meter bridge (Hewlett Packard 4284) in the frequency range 100 Hz -1 MHz at room temperature. The values of capacitance (C) and loss tangent (tanδ) were recorded by varying frequency at room temperature. The dielectric constant (ε′) was calculated by using the expression [George et al 2006, Gul et al 2007],

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (2)$$

Where C is the capacitance of pallet, d is the thickness of the pellet, A is the cross- sectional area of flat surface of pellet and ε_o is the permittivity of free space (ε_o= 8.85 x10^{-12} F-m^{-1}).

The dielectric loss tangent (tanδ) can be determined in terms of real and imaginary parts of dielectric constants using relation

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

Where ε″ and ε′ are the imaginary and real parts of the dielectric constants, respectively.

The AC conductivity of the samples was calculated from dielectric parameters using the relation [Hanumaian et al 1994]

$$\sigma = \varepsilon' \varepsilon_0 \omega \tan\delta \quad (4)$$

Where ω is the angular frequency.

Results and Discussion

DC Resistivity

The variation of DC resistivity versus temperature for all the samples is represented in Fig. 1. The resistivity of the samples decreases with increase in temperature indicating semiconducting behaviour. The plots are linear exhibiting three different regions separated by transition temperature T_1 and T_2. The lower transition temperature T_1 lies around 400K. The temperature T_2 at which point another break occurs coincides with the Curie temperature of the samples measured by initial permeability and AC susceptibility [Bachhav et al 2011]. The transition temperature T_1 and T_2 along with Curie temperatures for all samples determined by DC resistivity, initial permeability and AC susceptibility are enlisted in Table 1. The activation energies corresponding to three regions are calculated from slope of the resistivity (log ϱ) versus temperature (1000/T) graph. The activation energies corresponding to three regions are listed in Table. 2.

TABLE 1 DATA ON TRANSITION TEMPERATURE (K) AND CURIE TEMPERATURE (^{0}C) BY VARIOUS METHODS.

Composition (x)	Transition temperature (K)		Curie temperature (T_C) ^{0}C		
	T1	T2	By DC resistivity	By Permeability	By AC Susceptibility
0.1	400	516	236	240	243
0.2	375	526	252	257	253
0.3	413	538	270	275	265
0.4	425	606	325	314	333
0.5	421	630	355	360	357

Regarding the discontinuities in the resistivity verses temperature plots, Irkhin et al 2000 has stated that the change in the slope of the line occurs while passing through the Curie point where spin-spin interaction vanishes due to thermal vibrations. Such a discontinuity has also been reported by Ravinder et al 2000. The breaks in the conductivity plots are ascribed to the change in the conduction mechanism. Sankpal et al 1988 and many other researchers [Bhise et al 1992, Patil et al 1993, Patil et al 2000] have reported three regions of conductivity in case of Cu-Ni ferrite, of which the first region has been attributed to the presence of impurities, second region to phase transition and third region to the change in magnetic ordering. Patil et al 2000 has attributed these variations in conduction mechanism. The conduction at lower temperature is due to impurities while at higher temperatures it is due to the polaron hopping. In the present case, the slope is attributed to change in the conduction mechanism. The conduction in the first region is attributed to the presence of impurities while in second and third region to small polaron hopping. The second break occurring in the neighbourhood of the Curie temperature has been attributed to the influence of magnetic ordering on the conduction mechanism [Rao et al 1997].

Table. 2 shows compositional variation of DC resistivity at room temperature. The resistivity of the samples is found to increase with Ni content. The increasing trend of resistivity (ϱ) with Ni content can be attributed to the microstructural aspects. Addition of Ni decreases the grain size [Bachhav et al 2011]. The resistivity and the activation energies therefore rise as the Ni content increases.

Dielectric Properties

1) Dielectric Constant (ε') at Room Temperature with Frequency

The dielectric behaviour is one of the most important characteristics of ferrites which mainly depend upon preparation conditions, for instance. sintering time, quantity and type of additives. The dielectric constant (ε') results are due to heterogeneous structure of the material. The conducting ferrite grains are separated by thin layer of grain boundaries which are poorly conducting regions. The grain boundaries could be formed during sintering process due to superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere [Reddy et al 1982]. The grain boundaries of lower conductivity are effective at low frequencies while ferrite grains of high conductivity are effective at high frequencies [Koops et al 1951].

The variation of dielectric constant as a function of frequency at room temperature for all the samples in the frequency range 100 Hz-1 MHz is shown in Fig. 2. At low frequencies the values of dielectric constant are high and decrease rapidly with increases in frequency. Eventually, it attains a constant value which is the general trend for all ferrite samples [Ravinder et al 1999], which is due to the fact that the dielectric material exhibits induced electric moment under the influence of external electric field. At higher frequency, the polarization of the induced moments could not synchronize with frequency of applied electric field. As a result, the dielectric constant attains a constant value above certain high frequencies. As suggested by Koops et al 1951, the samples having heterogeneous structure contain well conducting grains separated by highly resistive thin grain boundaries, which causes localized accumulation of charge under the applied electric field building up space charge polarization. This is attributed to high dielectric constant at low frequency [Koops et al 1951, Maxwell et al 1954]. The electron reverses their direction with the increase of field reversal frequency of electric field. The probability of electron accumulation at grain boundaries are reduced thereby decreasing polarization. As a result, dielectric constant decreases with increase in

frequency and attains almost constant value. The decrease in ε' with frequency is because of the fact that any species contributively to polarizability is bound to show lagging behind applied field at higher and higher frequency.

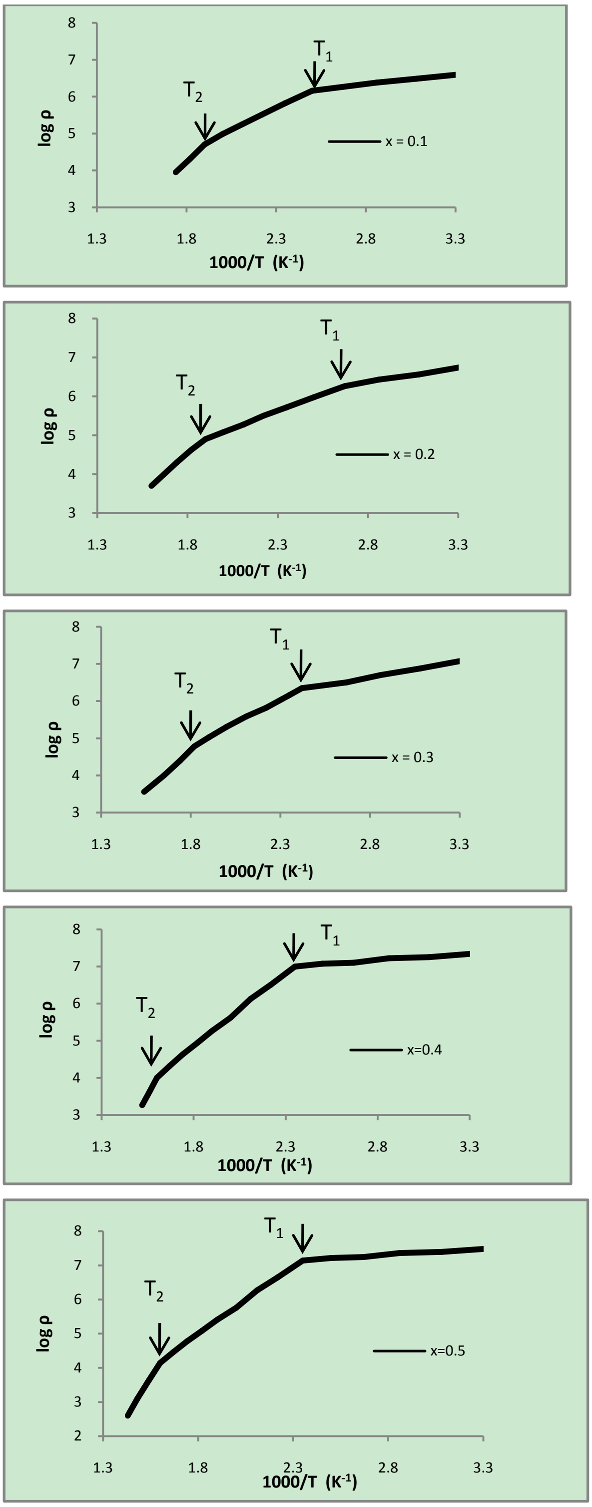

FIG. 1 VARIATION OF LOG RESISTIVITY WITH TEMPERATURE FOR $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ FERRITES

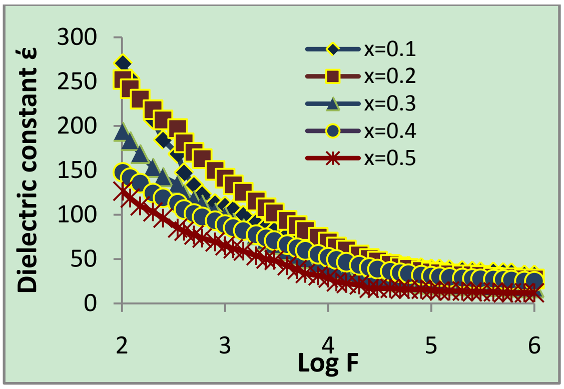

FIG. 2 VARIATION OF DIELECTRIC CONSTANT WITH LOG FREQUENCY FOR $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ FERRITES.

2) Dielectric Loss (tan δ) at Room Temperature with Frequency

The variation of dielectric loss tangent (tan δ) as a function of frequency for all the samples in the present system is shown in Fig. 3. It can be observed from the figure that tan δ decreases continuously with increasing frequency and attains constant value at higher frequencies and none of these samples exhibits the loss peak. The variation of dielectric constant with frequency reveals the dispersion due to Maxwell-Wagner [Maxwell et al 1954, Wanger et al 1913] type interfacial polarization in agreement with Koops phenomenological theory [Koops et al 1951] for the inhomogeneous double layer dielectric structure.

Iwauchi et al 1971 and Rezlescu et al 1974 having established a strong correlation between conduction mechanism and the dielectric behaviour of ferrites, have concluded that the electronic exchange between $Fe^{3+} \leftrightarrow Fe^{2+}$ results in the local charge displacement, which is responsible for polarization in ferrites. The magnitude of exchange depends upon the concentration of Fe^{2+} and Fe^{3+} ions on octahedral sites [Koops et al 1951, Reddy et al 1981].

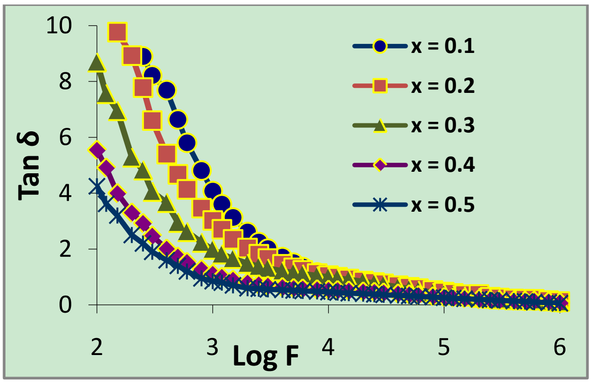

FIG. 3 VARIATION OF DIELECTRIC LOSS TANGENT WITH LOG FREQUENCY FOR $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ FERRITES.

3) Relation Between Dielectric Constant and DC Resistivity

The values of dielectric constant and DC resistivity are listed in Table 2. It can be observed from the table that the dielectric constant is inversely proportional to the square root of DC resistivity for those ferrite materials in which conduction mechanism plays fundamental role in the polarization process. The product $\varepsilon'\sqrt{\rho}$ remains nearly constant as mentioned in Table 2. Similar relationship between ε' and $\sqrt{\rho}$ has been observed by Ravinder et al 1999 and Ishaque et al 2010.

AC Conductivity

To confirm the conduction mechanism, AC conductivity was determined. The variation of AC conductivity with frequency for all samples is shown in Fig. 4. The graphs are almost linear representing that AC conductivity lifts with increase in frequency. In small polaron model, the conductivity increases linearly with rise in frequency [Patankar et al 2005, Patil et al 2008]. In present samples, the frequency dependence of AC conductivity indicates that the conduction is due to small polaron hopping mechanism which agrees with the values of activation energy obtained DC resistivity.

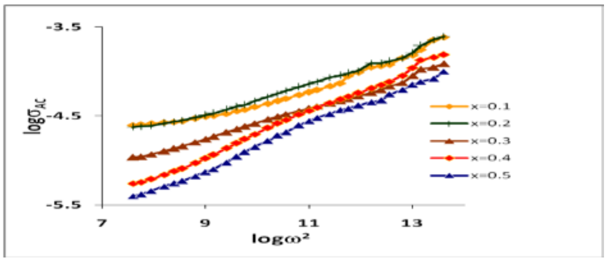

FIG. 4 VARIATION OF AC CONDUCTIVITY WITH LOG FREQUENCY FOR $Ni_xMg_{0.5-x}Cu_{0.1}Zn_{0.4}Fe_2O_4$ FERRITES

Conclusions

It has been observed with the substitution of Ni for Mg in the present samples, the DC resistivity, dielectric constant and AC conductivity are affected considerably. Temperature dependent DC electrical resistivity of the studied sample exhibits the semiconductor like behaviour and shows change in conduction behaviour at Curie temperature. An Mg concentration affects the activation energy. The variation in DC electrical resistivity is explained on the basis of Verwey's hopping mechanism. The values of dielectric constant are relatively high at low frequencies, which is attributed to the presence of interfacial polarization resulting from heterogeneous structure of material. The dielectric constant and dielectric loss tangent showed decreasing trend with increasing frequency, while the Curie temperature decreased with addition of nonmagnetic Mg ions contents. An AC conductivity rises with increase in frequency, which is normal behaviour of ferrites. The variation of AC conductivity with frequency is linear in nature suggesting that the conduction is due to small polaron hopping.

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TABLE 2 DATA ON ACTIVATION ENERGY (EV), DC RESISTIVITY (Ω-CM) AND DIELECTRIC CONSTANT (Ε')

Composition (x)	Activation energy (eV) Region I	Region II	Region III	DC resistivity (ϱ) x 106 (Ω-cm)	Dielectric constant (ε') (at 100Hz)	$\sqrt{\rho}$	$\varepsilon'\sqrt{\rho}$
0.1	0.10	0.35	0.50	4.04	271	2.0×10^3	5.4×10^5
0.2	0.15	0.47	0.65	5.82	252	2.4×10^3	6.0×10^5
0.3	0.18	0.50	0.74	12.59	194	3.5×10^3	6.8×10^5
0.4	0.08	0.78	0.98	22.53	148	4.7×10^3	7.0×10^5
0.5	0.14	0.85	1.12	31.11	110	5.5×10^3	7.0×10^5

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